ADVANCED MATERIALS

A Solution Chemistry Approach for the Selective Formation of Ultralong Nanowire Bundles of Crystalline Cd(OH)$_2$ on Substrates**

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Nanowires of different inorganic materials represent unique systems for exploring interesting nanoscale phenomena, and have consequently been synthesized with an eye towards applications in different fields.[1] Inorganic nanowires are also expected to play a critical role in future electronic and optoelectronic devices.[2] Since increasing emphasis has been placed recently on low cost, high throughput, high volume, and ease of production, various template-based syntheses have emerged as the method of choice for the synthesis of nanowires.[3] However, the main drawbacks associated with template-based methods arise from the production and removal of templates, and thus there has been a great deal of interest in developing template-less strategies. Furthermore, there are two prerequisites for the realization of nanodevices: the development of simple and economical methods for synthesizing nanomaterials in bulk quantities and the ability to control the dimensions of the nanostructures.[4]

In recent years, nanostructures of metal hydroxides such as Ni(OH)$_2$, Cu(OH)$_2$, Mg(OH)$_2$, and Cd(OH)$_2$ have been synthesized as potential templates or precursors for the corresponding oxide materials.[5] Among the various nanostructured metal hydroxides, Cd(OH)$_2$ is an important precursor for the eventual synthesis of functional materials such as CdS and CdSe by reaction with appropriate compounds. Previous reports of the synthesis of Cd(OH)$_2$ nanostructures in the literature include the preparation of nanowires,[6] nanodisks,[7] and nanoflakes.[8] A colloidal Cd solution obtained by the addition of an alkali solution to a cadmium salt (pH<10) has

been treated hydrothermally in an autoclave at elevated temperatures higher than 473 K. To synthesize Cd(OH)$_2$ nanorings, the Cd(OH)$_2$ precipitate obtained from the Cd salt has been irradiated using a highly intense ultrasonic horn.[9] Ichinose et al.[10] have reported the formation of Cd(OH)$_2$ nanostrands in water by raising the pH of the Cd-salt solution to 9. However, not much effort has been focused on studying the directed assembly and selective production of these nanostructures on substrates.

Here, we present a one-step, template-free, and seedless method for the selective growth of ultralong nanowire bundles of crystalline Cd(OH)$_2$ on glass substrates at low temperatures through a simple method involving controlled chemical precipitation based on principles of ionic and solubility products.[11] Through controlled precipitation, as the ionic product of the supersaturated solution exceeds the solubility product, the selective growth of nanowire structures occurs on the substrate via heterogeneous nucleation. In contrast, homogeneous nucleation proceeds in the solution phase. The chemistry involved in the formation of Cd(OH)$_2$ nanowires on substrate surfaces is discussed below.

The morphology and size of the as-synthesized Cd(OH)$_2$ nanostructures grown on glass substrates have been characterized by field-emission scanning electron microscopy (FESEM). A low-magnification FESEM image (Fig. 1a) shows that the products consist of a large quantity (100%) of nanowires with lengths ranging up to several tens of micrometers. The nanowires appear to be randomly distributed on the substrate surface with diameters ranging from 50 to 70 nm. Interestingly, a high-magnification FESEM image (Fig. 1b) reveals that the individual nanowires shown in Figure 1a are composed of several smaller nanowires that are aggregated into a bundle. The constituent smaller nanowires range from 7 to 10 nm in diameter, which is about a seventh to a tenth of the diameter of the thicker nanowire bundles. In contrast to the preferential formation of nanowire structures on the surface of the substrate, we have observed the formation of hexagonal plates with sub-micrometer dimensions along with nanowire bundles in the product powder obtained from the solution phase of the reaction bath (Fig. S1, Supporting Information).

Transmission electron microscopy (TEM) observations (Fig. 2a) indicate that the small nanowires, with diameters less than 10 nm, are aggregated together to form the bundle morphology, as suggested by the SEM results in Figure 1b. The high-resolution TEM (HRTEM) image of an individual small

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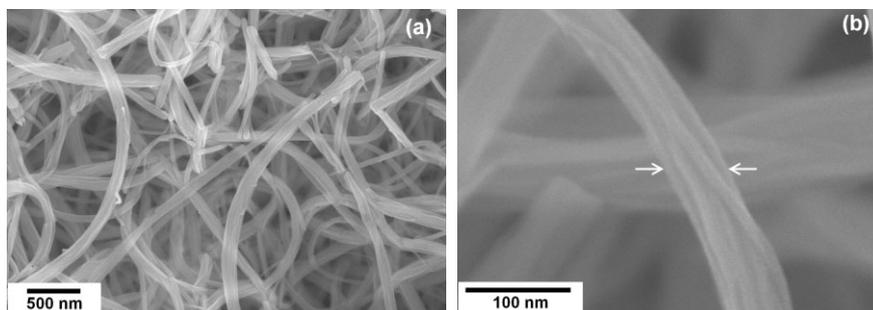Korea Basic Science Institute
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Figure 1. SEM images of Cd(OH)$_2$ nanowires deposited on a glass substrate at a) low and b) high magnifications.

Figure 2. TEM image of a) the nanowire bundle and b) HRTEM image of a single constituent nanowire.

erated from the interaction of Cd(OH)$_2$ with NO$_3^-$ anions in the solution. Since the concentration of NO$_3^-$ ions in the reaction bath is sufficiently high, these anions are likely to be incorporated into some of the crystalline Cd(OH)$_2$ via substitution of the –OH groups by nitrate ligands. However, no other morphology apart from nanowire bundles has been observed for cadmium hydroxide nitrate. The nitrate group can be easily eliminated by a chemical reaction or thermal treatment,[5a,12,13] for example, by anion exchange using NaOH solution, which leads to a reversible transformation between the two phases. Similar hydroxide formation has also been reported previously in the literature.[12–15] Fourier transform infrared (FTIR) investigations show that the nanowire bundles also contain NO$_3^-$ ions intercalated within the hydroxide phase (Supporting Information, Fig. S2).

It is worth noting that the selective formation of nanowire bundles has also been achieved on an indium tin oxide (ITO)-coated glass substrate, as well as on a Si substrate (Fig. S3, Supporting Information), suggesting that our method may be applicable to various substrate surfaces. Thus, an advantage of this method is that nanostructures can be grown on virtually any substrate material regardless of the shape of the substrate. This opens up opportunities for using these nanostructures in flexible electronics. Significantly, nanowire films ranging in thickness up to ca. 8 μm have been fabricated on the glass substrate (Supporting Information, Fig. S4), and the film thickness is readily controllable by simple changes in the synthesis conditions. For example, the diameter of the nanowires can be tuned by adjusting the concentration of the cadmium
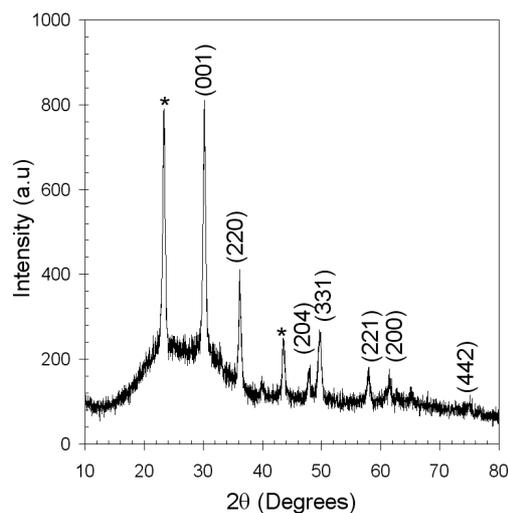
wire (Fig. 2b) indicates that the Cd(OH)$_2$ nanowires produced here have a crystalline structure. The inter-planar spacing has been measured to be about 0.248 nm, which is in good agreement with the (220) crystalline plane of monoclinic Cd(OH)$_2$. The phase identification of the sample deposited on the glass substrate has been further corroborated using X-ray diffraction measurements using CuKα1 radiation (λ = 1.5406 Å). As shown in Figure 3, the diffraction peaks are indexed to the monoclinic phase of Cd(OH)$_2$ with lattice constants of a = 6.530 Å, b = 10.223 Å, and c = 3.404 Å (Joint Committee on Powder Diffraction Standards (JCPDS) No. 40-0760). The peaks marked with an asterisk (*) are possibly from cadmium hydroxide nitrate (JCPDS No. 40-1491), which might be gen-


Figure 3. X-ray diffraction pattern of Cd(OH)$_2$ nanowires deposited on a glass substrate.

salt and the deposition period, as depicted in Figure 4, wherein the diameters of bundles and constituent nanowires appear to decrease with decreasing concentration of the Cd salt.
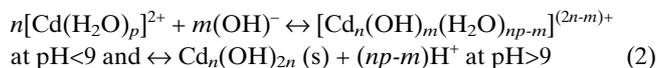
Our controlled precipitation method is based on the formation of a solid phase upon the transformation of a supersaturated solution to the saturated state. Two distinct steps, nucleation and subsequent particle growth, are involved in this process. During nucleation, clusters of metal precursor molecules likely undergo rapid decomposition. Subsequently the film grows to a certain thickness on the substrate surface by the coalescence of particles.[16] The preparation of $Cd(OH)_2$ nanomaterials in this work has been achieved by heating a supersaturated $Cd(NO_3)_2$ solution prepared by the addition of an NH_3 solution. The glass, ITO, or Si substrate is immersed in the solution during this process.

There are several possible soluble and insoluble Cd^{2+} species with ligands such as OH^-, H_2O, NO_3^-, and NH_3 in the reaction bath. For a solution containing cadmium nitrate salt with a concentration of ca. 0.1 M, Cd is soluble as hydrated Cd^{2+} at a pH value of 6 (Eq. 1).

$$nCd(NO_3)_2 + npH_2O \rightarrow$$
$$n[Cd(H_2O)_p]^{2+} + 2n(NO_3)^- \text{ at pH of ca. 6} \qquad (1)$$
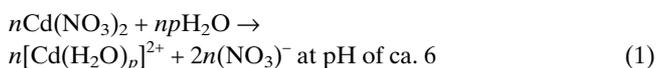
A soluble $Cd(NH_3)_q^{2+}$ complex is again produced at pH values higher than 12, whereas in the intermediate pH range between 6 and 12, insoluble $Cd_n(OH)_{2n}$ is formed since the pH of the solution affects the hydrolysis equilibrium by NH_3. However, the insoluble $Cd_n(OH)_{2n}$ is not the sole product obtained when NH_3 solution is added to the aqueous $Cd(NO_3)_2$ solution in the intermediat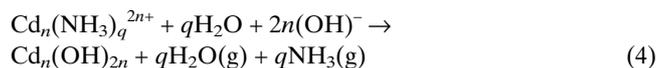e pH region. According to Ichinose et al.,[10] during the precipitation process, hydrated cadmium-ion complexes ($n[Cd(H_2O)_2]^{2+}$) are transformed to cadmium hydroxide ($[Cd_n(OH)_{2n}]$) via stepwise replacements of water molecules by hydroxide groups; this process is referred to as "olation", as depicted by Equation 2.

$$n[Cd(H_2O)_p]^{2+} + m(OH)^- \leftrightarrow [Cd_n(OH)_m(H_2O)_{np-m}]^{(2n-m)+}$$
at pH<9 and $\leftrightarrow Cd_n(OH)_{2n}$ (s) + $(np-m)H^+$ at pH>9 $\qquad (2)$

Upon further addition of the NH_3 solution, the white $Cd(OH)_2$ precipitate is dissolved and a clear solution is obtained at a pH value close to 12. The addition of the NH_3 solution reduces the $Cd(OH)_2$ precipitate by producing complex ions $Cd(NH_3)_q^{2+}$ with $q = 1$–4, where $q = 4$ is the most stable coordination number.[17] The formation of complex ions prevents spontaneous precipitation, leading to formation of a supersaturated state, as shown in Equation 3.

$$Cd_n(OH)_{2n} + qNH_4^+ + q(OH)^- \leftrightarrow$$
$$Cd_n(NH_3)_q^{2n+} + qH_2O + 2n(OH)^- \text{ at pH>12} \qquad (3)$$
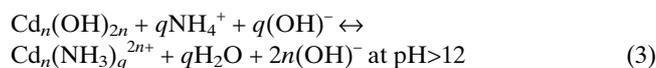
When this solution along with the immersed substrates is heated to 333 K, the solution once again becomes saturated (Eq. 4); the ionic product exceeds the solubility product by releasing H_2O and NH_3 and precipitation occurs via heterogeneous growth on the substrate (i.e., nanowire formation) as well as homogeneous growth in the solution phase (i.e., formation of hexagonal plates and nanowires).

$$Cd_n(NH_3)_q^{2n+} + qH_2O + 2n(OH)^- \rightarrow$$
$$Cd_n(OH)_{2n} + qH_2O(g) + qNH_3(g) \qquad (4)$$

Figure 4. FESEM images of $Cd(OH)_2$ nanowires obtained at different concentrations of the $Cd(NO_3)_2$ solution: a) 0.1 M, b) 0.075 M, c) 0.05 M, and d) 0.025 M.

An equilibrium state is established in the reaction bath after the solution becomes supersaturated. Upon heating this solution, the release of NH_3 and H_2O vapors from the reaction system disturbs the equilibrium and the pH of the reaction bath consequently decreases. In the earliest stages of the reaction, when the ionic product starts to exceed the solubility product, positively charged and highly anisotropic cadmium hydroxide nuclei are likely to be produced both on the substrate as well as in the solution. Such nuclei assemble together to form nanostrand structures with a high aspect ratio, as demonstrated elsewhere.[10,18] The surface charge of these nanostrands is likely to extremely positive and these structures are thermodynamically unstable. Thus, they serve as ideal building blocks and tend to assemble into ordered nanostructures. This is the beginning of the nucle-
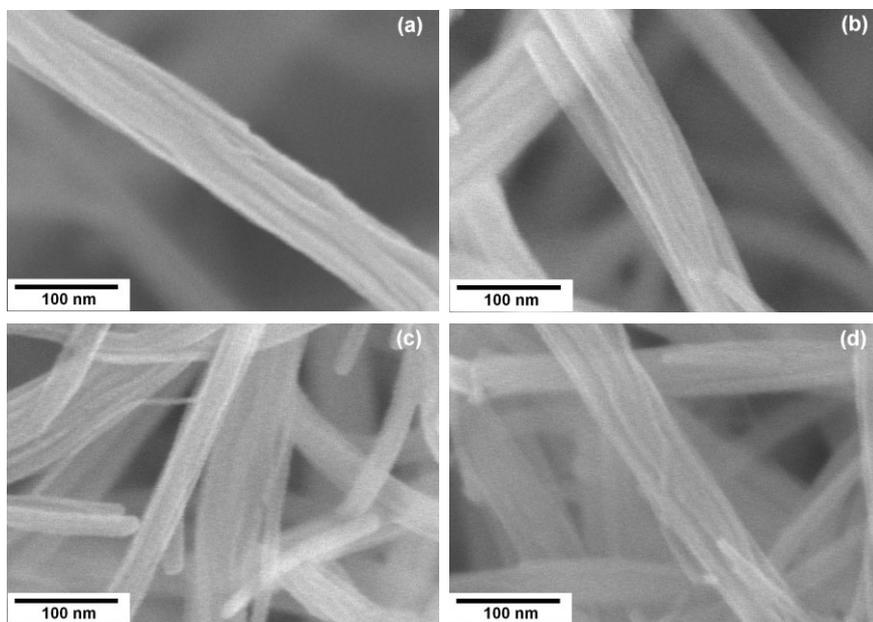
ation of the Cd(OH)$_2$ material, and subsequently these nano-strands grow as single wires on the substrates (e.g., Fig. S5a shows the morphology after a deposition period of 2 h, Supporting Information). In the next stage of the reaction, as the ionic product progressively increases, nanoparticles are collected on these single nanowires and collectively grow to form nanowire bundles (e.g., Fig. S5b shows the morphology after a deposition period of 4 h, Supporting Information). The bundles thus become thicker in diameter since the constituent nanowires progressively become thicker (e.g., Fig. 1 shows the morphology after a deposition period of 12 h). On the other hand, in the case of the homogeneous reaction in the bath, as these nuclei begin to grow, the different crystal planes of the nuclei have a different surface energy. Planes with higher energy surfaces have a strong tendency to capture smaller particles in order to reduce their surface energy. Thus, in solution the coalesced nanoparticles appear to grow predominantly in lateral directions to form a hexagonal plate-like shape by Ostwald's ripening process.[11] A small amount of nanowires are also formed, as illustrated in Scheme 1.

In conclusion, we have developed controlled precipitation chemistry as a method to prepare Cd(OH)$_2$ nanowires selectively on substrate surfaces. This method takes into account inherent differences in solubilities encountered during crystal formation. We have successfully demonstrated that reprecipitation leads to the direct formation of crystalline 1D nanomaterials on substrates. The size, surface coverage, diameter, and effective aspect ratio of the nanowires are readily tunable by modifying the metal salt concentration, deposition time, and temperature. This method may offer an elegant route for the direct growth of metal hydroxide nanowires on substrate surfaces with potential implications for attachment to electrodes for novel functional devices.
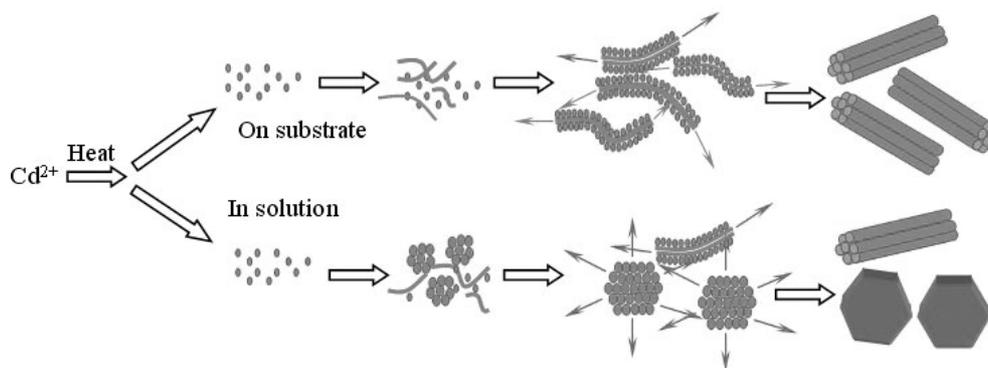
Experimental

An aqueous solution of 0.1 M Cd(NO$_3$)$_2$ (Aldrich Chemicals) was prepared, and to this solution aqueous NH$_3$ solution (28%) was added under constant stirring. A white precipitate was initially observed, which subsequently dissolved back into solution upon the further addition of the NH$_3$ solution. A pre-cleaned glass substrate was immersed and placed vertically in the solution. The solution was maintained at a pH of ca. 12 and a temperature of 333 K for 12 h, resulting in the direct growth of nanowire bundles on the glass substrate. The substrate with the deposited Cd(OH)$_2$ nanostructures was then removed from the Cd(NO$_3$)$_2$ aqueous alkaline bath, washed with deionized water, dried under air, and used for further characterization. An analogous experiment was peformed using CdCl$_2$ as the precursor. However, the formation of wires and/or bundles was not observed for these samples. The morphology and size of Cd(OH)$_2$ nanostructures deposited on the glass substrate were characterized by FESEM (XL30 ESEM FEG). For further insight into the microstructure of the nanowire bundles deposited on the glass substrate, TEM and HRTEM (H-9000NAR at 300 kV) observations were performed on these samples. The phase identification of the sample deposited on the glass substrate was further investigated using a Rigaku X-ray diffractometer for thin films using CuKα1 radiation (λ = 1.5406 Å). FTIR transmission spectra were measured on a Nicolet model Imapact 400D FTIR spectrometer (KBr pellets, 4 cm^{-1} resolution).

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Scheme 1. Schematic depiction of the selective formation of Cd(OH)$_2$ nanowire bundles on the substrate and hexagonal plates in the solution phase from a supersaturated alkaline Cd(NO$_3$)$_2$ solution.

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